

Higher-order glass-transition singularities in systems with short-ranged attractive potentials

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Abstract. Within the mode-coupling theory for the evolution of structural relaxation, the A_4 glass-transition singularities are identified for systems of particles interacting with a hard-sphere repulsion complemented by different short-ranged potentials: Baxter's singular potential regularized by a large-wave-vector cutoff, a model for the Asakura-Oosawa depletion attraction, a triangular potential, a Yukawa attraction, and a square-well potential. The regular potentials yield critical packing fractions, critical Debye-Waller factors and critical amplitudes very close to each other. The elastic moduli and the particle's localization lengths for corresponding states of the Yukawa system and the square-well system may differ by up to 20% and 10%, respectively.

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1. Introduction

In this paper, some results shall be presented for the liquid-glass-transition diagrams of simple systems as obtained within the mode-coupling theory for the evolution of structural relaxation (MCT) [1]. This theory is based on closed non-linear equations of motion for the normalized autocorrelation functions for density fluctuations with wave-vector modulus $q = |\vec{q}|$, $\phi_q(t)$. Liquid states are characterized by solutions vanishing for large times t , $\phi_q(t \rightarrow \infty) = 0$. Glasses are characterized by solutions whose long-time limits are the non-vanishing Debye-Waller factors of the arrested amorphous structure $f_q = \phi_q(t \rightarrow \infty)$, $0 < f_q \leq 1$. The f_q obey the set of implicit equations

$$\frac{f_q}{1 - f_q} = \mathcal{F}_q[f_k]. \quad (1a)$$

The mode-coupling functional \mathcal{F}_q reads

$$\mathcal{F}_q[f_k] = \sum_{\vec{k} + \vec{p} = \vec{q}} V(\vec{q}, \vec{k}, \vec{p}) f_k f_p \quad (1b)$$

with coupling coefficients

$$V(\vec{q}, \vec{k}, \vec{p}) = \rho S_q S_k S_p \{ [\vec{k} c_k + \vec{p} c_p] \vec{q} / q \}^2 / (2q^2). \quad (2)$$

Here, S_q and c_q are the structure factor and the direct correlation function, respectively, related by the Ornstein-Zernicke equation $S_q = 1/[1 - \rho c_q]$. The structure factor depends on control parameters like the particle density ρ , the temperature T , and parameters specifying the dependence of the interaction potential $U(r)$ on the

interparticle distance r . Let us combine the set of control parameters considered to a control-parameter vector \mathbf{V} . The discussion will be restricted to parameter regions where S_q , and hence \mathcal{F}_q , depend smoothly on \mathbf{V} . The Debye-Waller factor f_q for a given \mathbf{V} is distinguished from possible other solutions of Equations (1,2) for the same \mathbf{V} , say \tilde{f}_q , by the maximum property: $f_q \geq \tilde{f}_q$ for all q .

For almost all control parameters, the Debye-Waller factors f_q depend smoothly on \mathbf{V} . The exceptional points are referred to as glass-transition singularities \mathbf{V}^c . These critical points of Equations (1,2) are bifurcation singularities of the cuspid family A_l , $l = 2, 3, \dots$. An A_l bifurcation describes a topologically stable singularity that is equivalent to the bifurcation singularities of the zeros of a real polynomial of degree l [2]. The liquid-glass transition points are A_2 singularities located on smooth surfaces in parameter space. If \mathbf{V} crosses this surface at some \mathbf{V}^c , the long-time limit $\phi_q(t \rightarrow \infty)$ jumps from zero to the critical Debye-Waller factor $f_q^c > 0$. There may exist surfaces of A_2 singularities within the glass. These describe iso-structural transitions from one amorphous state characterized by $f_q > 0$ to another state specified by a larger Debye-Waller factor $f_q^c > f_q$. For every A_2 singularity, a number λ , $0.5 \leq \lambda < 1$, can be calculated. It is called the exponent parameter since it determines the various anomalous exponents entering the description of the slow dynamics for \mathbf{V} near \mathbf{V}^c . The higher-order singularities, A_l , $l \geq 3$, are the endpoints of the transition surfaces characterized by $\lambda = 1$. In the following, some properties of A_4 singularities \mathbf{V}^* shall be discussed. Interparticle interactions shall be considered consisting of a hard-sphere-repulsion core of diameter d and a short-ranged attraction potential for $r > d$. The latter shall be parameterized by a typical attraction strength u_0 and a typical attraction range Δ . Therefore, a three-dimensional control-parameter space is considered: $\mathbf{V} = (\varphi, \Gamma, \delta)$, where $\varphi = (\pi/6)\rho d^3$ denotes the packing fraction of the spheres, $\Gamma = u_0/(k_B T)$ is a dimensionless attraction strength or an inverse dimensionless temperature, and $\delta = \Delta/d$ is an attraction-range parameter.

For a system of particles interacting with a hard-sphere repulsion complemented by a short-ranged attraction, MCT leads to two intriguing results [3, 4]. First, the increase of the attraction strength Γ may cause a melting of the glass. This implies a reentry phenomenon for the transition diagram. For certain values of the packing fraction φ , the liquid freezes into a glass not only by cooling but also by heating. This prediction has been verified recently for colloidal suspensions [5, 6]. In this work, the parameter Γ was varied by adding polymer to the solvent thereby increasing the strength of the depletion attraction. The reentry phenomenon was also established by molecular-dynamics-simulation studies [5, 7, 8, 9]. Second, the existence of an A_3 singularity was predicted. The glass-glass transitions connected with this higher-order singularity deal with discontinuous changes of the localization mechanism from one caused by the repulsion-induced cage effect to one caused by the attraction-induced bonding of the particles. The cited work was based on Baxter's model for sticky hard spheres (SHS) [10] complemented with a large cutoff wave vector q_{co} restricting the wave-vector sums in the mode-coupling functional from Equation (1b). The effective range of the regularized potential introduced by the cutoff can be parameterized by $\Delta = \pi/q_{co}$. The singular Baxter interaction leads to a large- q -tail for the direct correlation function $c_q = \mathcal{O}(1/q)$. It is this tail for $2\pi/d < q < q_{co}$ that causes the A_3 bifurcation. This A_3 singularity disappears if q_{co} is decreased towards $2\pi/d$.

The generic scenario for the disappearance of an A_3 singularity in a three parameter system is the existence of an A_4 glass-transition singularity at some point $\mathbf{V}^* = (\varphi^*, \Gamma^*, \delta^*)$. Thus, the cited results [1, 2, 3, 4] lead to the following conclusion.

A system of particles interacting with some steep strong repulsion core complemented by a sufficiently strong short-ranged attraction potential exhibits an A_4 singularity at some control-parameter point \mathbf{V}^* . The general transition diagram is organized around this \mathbf{V}^* . Diagrams for different models for the interparticle interaction can be mapped onto each other for small $\mathbf{V} - \mathbf{V}^*$ by a smooth invertible parameter transformation. In this sense, the bifurcation scenario is universal. The scenario at an A_4 singularity has been demonstrated in some detail for the square-well system [11]. In the following, these results shall be extended and compared with the ones calculated for other potentials that might be of interest for the description of colloidal systems.

2. Results

Let us specify the attraction potentials to be considered and the approximation theories to be used to evaluate S_q . The model of SHS complemented by the mentioned cutoff q_{co} shall be used with the convention $\Gamma = 15/\tau$. For the definition of the stickiness parameter τ and the evaluation of the structure factor we follow Baxter's work [10]. The hard-core Yukawa system (HCY) is used with the following convention for the control parameters

$$U(r)/(k_B T) = -\Gamma \exp[-(r-d)/(\delta d)]/(r/d), \quad d < r, \quad (3)$$

i.e., δ is chosen as the inverse of the conventional screening parameter b . The structure factor is evaluated analytically in the mean-spherical approximation [12]. Furthermore, three potentials of polynomial shape are considered:

$$U(r)/(k_B T) = -\Gamma[(d + \delta d - r)/(\delta d)]^{(n-1)}, \quad d < r < (1 + \delta)d. \quad (4)$$

For $n = 1$, the formula describes the square-well system (SWS). The triangular-potential model (TRI) is obtained for $n = 2$. The Asakura-Oosawa system (AOS) is modelled by $n = 3$. The latter potential is obtained as small- δ limit for the depletion attraction acting between spheres in a dilute solvent of small polymers [13]. It was shown that the equations for the mean-spherical approximation for S_q of the SWS can be solved analytically by an expansion in δ [11]. This procedure can be extended to treat the potentials of Equation (4) for every n . The leading order expansion formulae are noted in Appendix A, and they are used in the following. Let us recall, that for the range of length-parameters of interest, say $\delta < 0.20$ for the SWS, the next-to-leading-order result is very close to the full numerical solution for $n = 1$ [11].

To determine f_q for a given \mathbf{V} , the standard iteration procedure is applied: $f_q^{(n)}/(1 - f_q^{(n)}) = \mathcal{F}_q[f_k^{(n-1)}]$, $n = 1, 2, \dots$, $f_q^{(0)} = 1$, $\lim_{n \rightarrow \infty} f_q^{(n)} = f_q$ [1]. This is done after Equations (1,2) are rewritten so that the wave-vector moduli are discretized to M points on a grid of equal spacing h . The values $h = 0.4/d$ and $M = 300$ have been used to identify the A_2 singularities on the bifurcation surface. It is cumbersome to identify the higher-order singularities since $(l - 1)$ control parameters have to be scanned and the convergence of the iteration is slower for points at an A_{l+1} singularity than at an A_l one. One can use the deviation of λ from unity to characterize the error for the identification of an A_l with $l \geq 3$. In our calculations we achieved $1 - \lambda < 10^{-3}$. At the end, the calculation at \mathbf{V}^* was repeated with $h = 0.08/d$ and $M = 1500$ in order to check the independence of the results from the discretization approximation.

As a representative example, figure 1 exhibits the glass-transition-singularity diagram of the HCY. The inner points of the lines are A_2 singularities obtained as constant- δ cuts through the bifurcation manifold in the three-dimensional space of

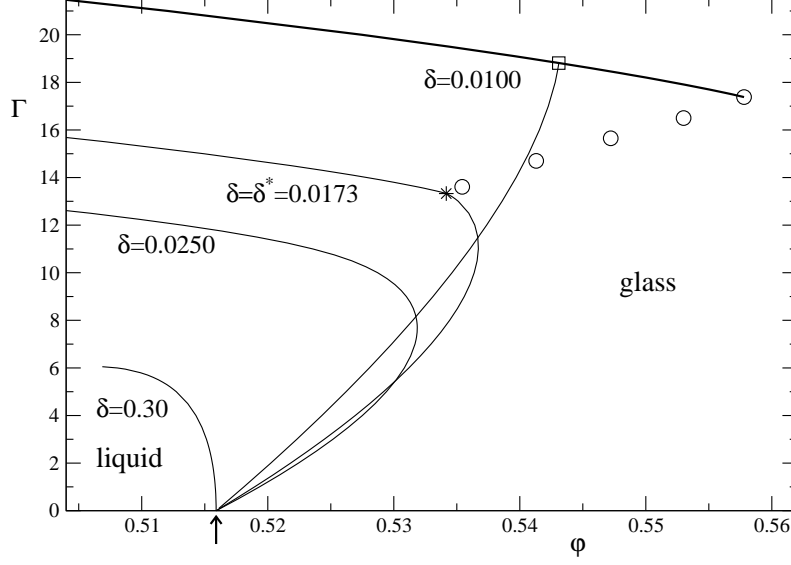


Figure 1. Transition diagram for the hard-core-Yukawa system (HCY). The attraction strength Γ versus packing-fraction φ curves show cuts through the surfaces of glass-transition singularities for fixed attraction-range parameter δ as indicated; cf. Equation (3). The line for $\delta = \delta^* = 0.0173$ hits the A_4 singularity (*). The line for $\delta = 0.0100$ exhibits a crossing point (□), and an A_3 singularity (○). Four further A_3 singularities are marked by circles; they refer from left to right to $\delta = 0.0167, 0.0143, 0.0125, 0.0111$. The arrow points to the critical packing fraction $\varphi_{\text{HSS}}^c = 0.516$ for the hard-sphere system.

control parameters \mathbf{V} . There are three topologically different cuts. The smooth line shown for $\delta = 0.0250$ represents a typical cut for $\delta > \delta^*$. All points describe liquid-glass transitions characterized by an exponent parameter $\lambda < 1$. For $\delta = \delta^* = 0.0173 \dots$, the transition line runs through the A_4 singularity marked by a star. For all $\mathbf{V} \neq \mathbf{V}^*$, the line is smooth and $\lambda < 1$. For $\mathbf{V} = \mathbf{V}^*$, $\lambda = 1$ and the line has a continuous tangent but an infinite curvature. The lines for $\delta < \delta^*$ consist of two pieces as demonstrated for $\delta = 0.0100$. The part shown as a heavy line with $d\Gamma^c/d\varphi^c < 0$ terminates within the glass in an A_3 singularity marked by a circle. The second part shown as a light line terminates in a crossing point indicated by a square. The line of A_2 singularities between the crossing point and the A_3 singularity deals with glass-glass transitions and the other part with liquid-glass transitions. A_2 -glass-transition curves for the HCY for $\delta \neq \delta^*$ cuts have been considered previously for the HCY [4, 14, 15].

Let us add a remark on the diagram. Obviously, for $\Gamma = 0$, all cuts start at the critical packing fraction of the hard-sphere system (HSS), $\varphi_{\text{HSS}}^c = 0.516$. There is a characteristic range parameter δ_{reentry} so that the slope $d\Gamma^c/d\varphi^c$ for $\Gamma = 0$ is negative for $\delta > \delta_{\text{reentry}}$ and positive for $\delta < \delta_{\text{reentry}}$. The latter case is exemplified in figure 1 by the three cuts discussed in the preceding paragraph, the former case is shown by the cut for $\delta = 0.300$. For $\delta < \delta_{\text{reentry}}$ and sufficiently small Γ , the transition curves deal with melting of the glass upon increasing the attraction parameter Γ . Hence, for all liquid states with $\varphi > \varphi_{\text{HSS}}^c$, one gets the reentry phenomenon mentioned in the introduction. The bonding forces create holes in the cages and this can destroy the particle localization for long times. In agreement with Lindemann's melting criterion,

the critical localization length of the HSS is about $r_s^c = 0.0746d$. If the attraction-potential range Δ is much larger than r_s^c , i.e., if δ exceeds a critical value δ_{reentry} , the bonding effects cannot change the cage structure. Therefore, the reentry mechanism disappears for $\delta > \delta_{\text{reentry}}$. In this case, the transition curve is similar to the one obtained for a typical van-der-Waals system described, e.g., by a Lennard-Jones potential. One obtains $\delta_{\text{reentry}} = 0.30$ and 0.117 for HCY and SWS, respectively. It should be noted that the transition curve shown for $\delta = 0.30$ terminates at the spinodal line defined by the divergence of S_q for $q = 0$. Beyond this point, MCT equations are meaningless and calculations of density correlators cannot be performed there within that theory.

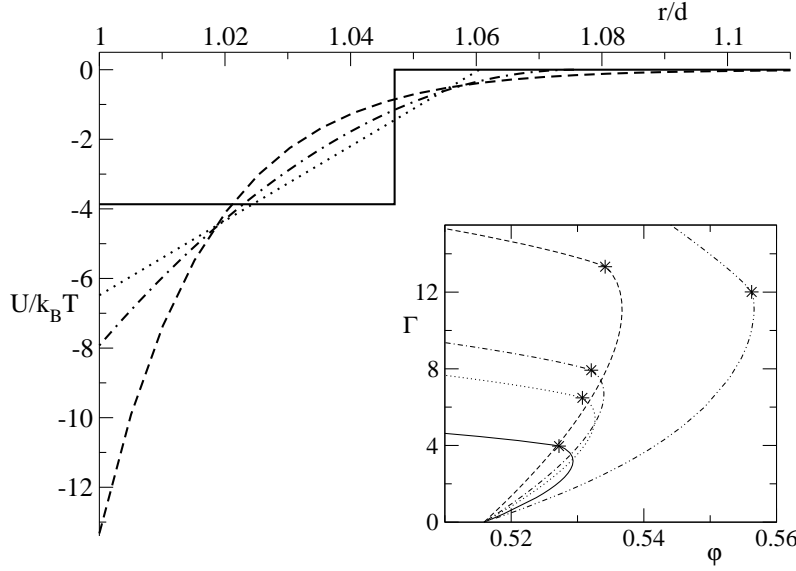


Figure 2. Attractive potentials U relative to the thermal energy $k_B T$ as function of the interparticle distance r relative to the hard-sphere diameter d for control parameters V^* at the respective A_4 singularity. The curves refer to the SWS (—), TRI (···), AOS (— · —), HCY (---) and SHS (— · · · —). The inset shows the cuts of the bifurcation surfaces through \mathbf{V}^* for fixed attraction-range parameter $\delta = \delta^*$.

Figure 2 exhibits the four regular attraction potentials defined in Equations (3,4) for control parameters at the respective A_4 singularities. The inset shows cuts through the liquid-glass-transition surfaces for fixed range parameter δ^* . The regular potentials are rather close to each other for $1.01 \leq r/d \leq 1.05$. The volume of the shell $1.00 < r/d < 1.02$ is smaller than the one for the shell $1.02 < r/d < 1.04$. Within the latter, the attraction strength decreases in the sequence SWS, TRI, AOS and HCY. Therefore, the critical packing fraction ϕ^* for the onset of an iso-structural glass transition increases in this sequence. One finds $\phi^* = 0.5272, 0.5307, 0.5321$, and 0.5342 , respectively. For the same reason, the maximum packing fraction of the liquid increases in this sequence. One gets $\phi^{\text{max}} = 0.5293, 0.5326, 0.5340$, and 0.5367 , respectively. For Baxter's model, all mode-coupling effects have been cut off for $q > \pi d/\delta^*$. Therefore, the bonding effects are reduced compared to those for the regular potentials and the values $\phi^* = 0.5562$ and $\phi^{\text{max}} = 0.5566$ for the SHS are larger than the corresponding values for the regular potentials. Evaluating the

structure factor of the SWS up to next-to-leading order as done in Reference [11], one gets $\varphi^* = 0.5277$ and $\varphi^{\max} = 0.5299$. Indeed, the difference of these numbers from those calculated with the formulae from Appendix A is small.

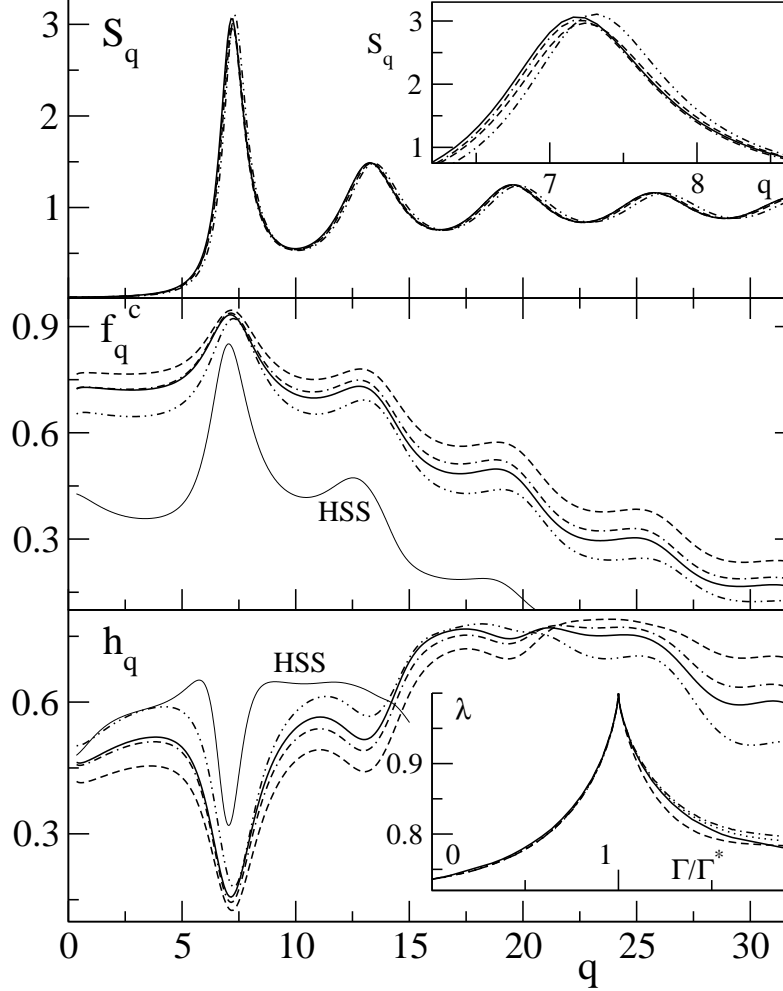


Figure 3. Structure factor S_q , critical Debye-Waller factor f_q^c , and critical amplitude h_q for control parameters specifying the A_4 singularity V^* , SWS (—), HCY (---) and SHS (-·-·-·-). The fourth curve (----) shows the results for the SWS using the structure-factor up to next-to-leading order in δ [11]. The lines denoted by HSS exhibit f_q^c and h_q for the critical point of the hard-sphere system. The inset from the lower panel shows the variation of the exponent parameter λ along the liquid-glass transition lines through V^* from Figure 2.

Structure factors S_q at the A_4 singularities and the corresponding critical Debye-Waller factors f_q^c are compared in Figure 3. Also compared are the so-called critical amplitudes h_q . These are evaluated by a straightforward but involved procedure from the mode-coupling functional at the bifurcation point [1]. They quantify the susceptibility of the arrested structure. The increase of $(f_q - f_q^c)$ upon increasing $V - V^*$ is proportional to h_q and so is the prefactor in the logarithmic decay laws

that are the characteristic feature of the dynamics near a higher-order singularity [16]. S_q for various models mainly differ by a small shift parallel to the q -axis only. This shift reflects the decrease of the interparticle distance caused by the increase of φ^* . The f_q^c oscillate in phase with S_q and the h_q oscillate in opposite phase as known and explained for the simple HSS [1]. However, the f_q^c are considerably larger and the h_q are smaller than the corresponding quantities at the hard-sphere transition. This is a manifestation of the fact that the attractive part of the potential enforces localization, provided a glass state is established. Within the wave-vector region around the first diffraction peak, say $1 \leq qd \leq 10$, the Debye-Waller factor of the SWS differs from the one of the HCY up to about 7% while this difference is minimal at the peak. The corresponding difference for the critical amplitude is about 9% which is maximal at the peak. The inset for the lowest panel of Figure 3 displays the variation of the exponent parameter λ for the liquid-glass transitions on the cuts $\delta = \delta^*$. Rescaled as a function of Γ/Γ^* , the λ cannot be distinguished on the branch $\Gamma/\Gamma^* < 1$ dealing with transitions to the repulsion dominated glass. On the branch $\Gamma/\Gamma^* > 1$, which deals with transitions to the attraction dominated glass, the λ for the various models are still very close to each other.

Figure 3 also exhibits results for the SWS evaluated with the structure factor in next-to-leading order of Reference [11] in comparison with those based on the leading order theory explained in Appendix A. Obviously the difference is too small to be of interest.

The macroscopic mechanical stiffness of liquids and glasses is quantified by the elastic moduli. The longitudinal modulus M_L specifies the stiffness for compressions and the transversal one M_T , also called shear modulus G' , the stiffness for shear deformations. They are defined as constants of proportionality in the linearized stress-strain relation. In systems with Newtonian microscopic dynamics, they determine the speed of longitudinal and transversal sound, respectively, via $v_{L,T} = \sqrt{M_{L,T}/(\rho m)}$ with ρm denoting the mass density. For an ergodic system, the shear modulus vanishes, $M_T^0 = 0$. The longitudinal modulus reads $M_L^0 = \rho(k_B T) S_0^{-1}$ with $S_0 = \lim_{q \rightarrow 0} S_q$. In the glass state, the moduli are larger: $M_{L,T} = M_{L,T}^0 + \delta M_{L,T}$. The additional contributions are the positive long-time limits of fluctuating-force correlators. For the latter, MCT yields [1]:

$$\delta M_{L,T} = \rho(k_B T) \lim_{q \rightarrow 0} \sum_{\vec{k} + \vec{p} = \vec{q}} S_k S_p f_k f_p \{ [\vec{k} c_k + \vec{p} c_p] e_{\vec{q}}^{\mathcal{L},T} \}^2 (\rho/2q^2). \quad (5)$$

Here $e_{\vec{q}}^{\mathcal{L},T}$ are unit vectors parallel and perpendicular to \vec{q} , respectively. The limit leads to

$$\delta M_{L,T} = \rho(k_B T) \int_0^\infty dk \{ \rho [S_k f_k k / (2\pi)]^2 w_{L,T}(k) \}, \quad (6a)$$

$$w_L(k) = c_k^2 + \frac{2}{3} (k c'_k) c_k + \frac{1}{5} (k c'_k)^2, \quad (6b)$$

$$w_T(k) = \frac{1}{15} (k c'_k)^2. \quad (6c)$$

In Figure 4 the moduli for the SWS are compared with the ones for the HCY. The states are chosen on the cuts $\delta = \delta^*$ through the respective transition surface. The compression modulus M^0 of the liquid varies smoothly throughout reflecting the well known increase of the compressibility with increasing attraction forces. The large variations of $\delta M_{L,T}$ reflect the strong effect of bonding potentials on restoring forces

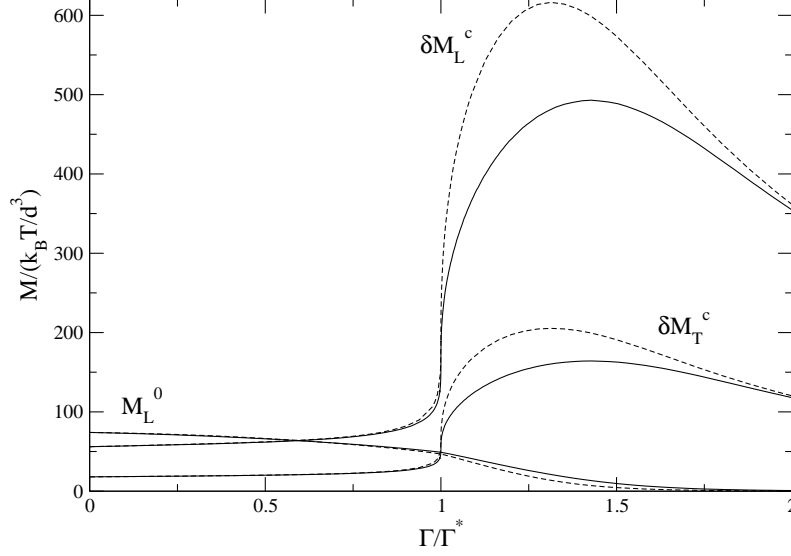


Figure 4. Longitudinal elastic moduli M_L and transversal elastic moduli M_T for the $\delta = \delta^*$ transition line of the SWS (HCY) shown as full (dashed) lines. For the SWS, the structure factor from [11] was used. In the limiting case of the HSS, $M_L^0 = 74.1$, $\delta M_T = 18.1$, $\delta M_L = 56.1$. At the A_4 singularity for the SWS (HCY), $\delta M_T^* = 54.3(64.4)$, $\delta M_L^* = 163.4(193.6)$. At the maximum $\delta M_T = 164.2(205.3)$, $\delta M_L = 493.0(616.3)$.

[4, 11]. The same bonds are resisting shear as well as compression deformations. Therefore, there is no great difference in the behaviour of the two moduli. The contributions to δM_L due to the first two terms in Equation (6b) are smaller than the one due to the last term. Further, incidentally, these two contributions nearly cancel. Therefore, δM_L^c differs from $3\delta M_T^c$ by less than 3% for $\Gamma < \Gamma^*$ and less than 0.5% for $\Gamma \geq \Gamma^*$. The universal properties of the A_4 bifurcation imply the following: The moduli vary smoothly for all $\Gamma \neq \Gamma^*$ and at the A_4 singularity there is a cubic-root singularity: $M(\Gamma) - M(\Gamma^*) \propto (\Gamma - \Gamma^*)^{1/3}$. The singular increase of M with Γ increasing through Γ^* is a precursor of the discontinuous increase of M upon crossing the glass-glass-transition line for $\delta < \delta^*$. If Γ increases further, the moduli have to decrease since the density decreases towards zero. Therefore, the moduli exhibit a maximum at some value of Γ exceeding Γ^* . By continuity, such maximum also occurs for cuts with δ close but not equal to δ^* , as was noticed before for the shear modulus [4, 17].

The clearest quantity for demonstrating the change of the glassification mechanism upon increasing the attraction, is the variation of the particle's localization length r_s as a function of Γ for states on the cut $\delta = \delta^*$ (Figure 5). This length is given by the mean-squared radius of a particle's long-time probability density. The Fourier-transform of the latter is the Lamb-Mössbauer factor f_q^s that is evaluated from an equation similar to Equation (1) [1]. One ends up with an equation for the inverse of r_s^2 analogous to the equations for the moduli:

$$1/r_s^2 = \frac{1}{6} \int_0^\infty dk \{ \rho S_k f_k f_k^s [c_k k^2 / \pi]^2 \}. \quad (7)$$

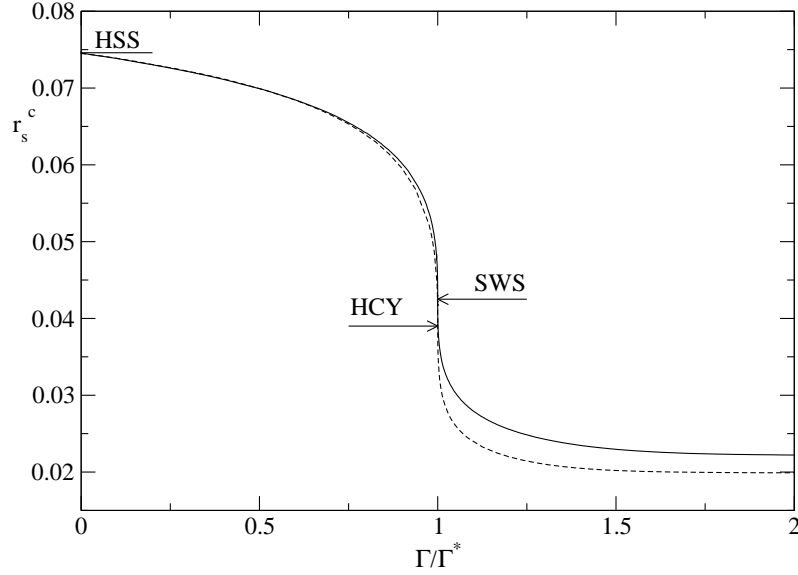


Figure 5. Localization length r_s^c of a tagged particle for states on the $\delta = \delta^*$ transition line for the SWS (HCY) shown as full (dashed) line. At the A_4 singularity one gets $r_s^c/d = 0.0425(0.0390)$ as indicated by the arrows. The line labeled HSS marks the localization length $r_s^c/d = 0.0746$ for the HSS.

With increasing Γ , r_s^c decreases monotonously from the value for the HSS, $r_s^c/d = 0.0746$. The variation is smooth except for the cubic-root singularity at $\Gamma = \Gamma^*$. For strong bonding, r_s^c decreases to a Γ insensitive value of the order of the attraction potential range, as noted before for $\delta > \delta^*$ in the HCY [4].

3. Discussion

The first peculiarity of structural relaxation in systems of particles interacting with hard-sphere-like repulsions complemented by short-ranged attractions predicted by mode-coupling theory (MCT) [3, 4], namely the reentry phenomenon for the liquid-glass-transition diagram, has been established recently [5, 6, 7, 8, 9]. This justifies to focus now on the more difficult task of testing the second prediction concerning the existence of A_3 and A_4 singularities. The signature of such higher-order singularities is the extreme stretching of relaxation curves as has been explained on the basis of asymptotic expansions in terms of powers of logarithms in time [16]. The recent simulation results [7, 9] provide hints that there are such logarithmic decay laws. However, a more detailed analysis of the data would be required if one intends to arrive at compelling conclusions. The transition diagram exhibiting A_3 singularities is organized around an A_4 singularity. So far, such singularity was identified within a microscopic theory only for the square-well system [11]. For this system, all parameters and amplitudes necessary for a discussion of the logarithmic decay laws have been evaluated [18]. In the present paper, A_4 singularities have been identified and characterized for a series of other attraction potentials in order to provide some information on the sensitivity of the MCT results on the microscopic details assumed for the interaction.

The critical packing fractions φ^* found for the A_4 singularities of the four regular potentials considered (Figure 2) or the related largest values for the liquid packing φ^{\max} exceed the critical packing fraction φ_{HSS}^c of the hard-sphere system by about 3%. But the difference between these values for different models is about 1.4% only. It is not clear, whether or not experiments can discriminate between the φ^* or φ^{\max} predicted for, say, SWS and HCY. But simulation studies for the diffusivity of the kind published recently [8, 9] should be able to test our prediction $\varphi_{\text{HCY}}^{\max} > \varphi_{\text{SWS}}^{\max}$.

The singular potential for sticky hard spheres was introduced by Baxter [10] as a certain attraction-range-to-zero limit in order to simplify equations from a mathematical point of view. But, within MCT, these simplifications cannot be made use of since the limit to zero for the range parameter δ must not be permuted with the limit to infinity for the wave vectors in the mode-coupling integrals. The problem can be handled by introducing some wave-vector cutoff [3, 4]. This is equivalent to introducing a regular potential leading to a considerably larger $\varphi^* - \varphi_{\text{HSS}}^c$ than found for the other potentials examined above.

It is well known that the structure factor theories used in this paper lead to unsatisfactory results for the thermodynamic functions. Great progress has been made to improve on this point as is discussed, e.g., in Reference [14]. The thermodynamic functions are derived from the zero-wave-vector limits of correlators. However, different from the limit of large wave vectors, which is important to capture the essential physics of the glass transition, small- q effects play a minor role for the transition curves. As already demonstrated for the SWS in [11], artificially setting the structure factor input to zero for $qd < 4$ does not alter the transitions qualitatively. For $\Gamma \gtrsim \Gamma^*$ where large q values dominate, transition lines are in accordance even quantitatively.

The differences among the structure factors of the various models for wave vectors accessible in scattering experiments for colloids, say $2 \leq qd \leq 15$, are very small if the states at the A_4 singularity are compared (Figure 3). However, the differences between the Debye-Waller factors and the critical amplitudes are of the order of 5%. The f_q^c and h_q determine the amplitudes of the leading-order formulae for the intermediate scattering functions for states near an A_4 singularity in a similar manner as they determine the corresponding results near an A_2 liquid-glass transition [16]. If they could be deduced from a data analysis with similar accuracy as one can do from data near an A_2 singularity, one could discriminate, e.g., between the square-well model and the hard-core-Yukawa system.

The tagged particle localization is described by the Lamb-Möbbauser factor, f_q^s , that can be measured by incoherent scattering. It is a bell-shaped function of q and its width can be quantified by the localization length r_s : $f_q^s = 1 - (qr_s)^2 + \mathcal{O}(q^4)$. As expected from the shape of the attractive potentials at the A_4 singularity (Figure 2), r_s^* is smaller for the HCY than for the SWS by 10%. The MCT brings out that r_s^c becomes insensitive to Γ for strong attraction. For the SWS (HCY) one gets $r_s^c/d = 0.022$ (0.020) for $\Gamma/\Gamma^* > 1.8$ within 1% accuracy.

The largest difference between SWS and HCY is found at the maximum of the elastic moduli where the HCY is about 20% stiffer than the SWS. Taking the critical moduli of the HSS as reference, the maxima of SWS and HCY should be at 9 or 11 times that value, respectively, as shown in Figure 4.

The line of glass-glass transitions occurring for the cuts through the bifurcation surface for $\delta < \delta^*$ has some analogue in the line of iso-structural phase transitions from one face-centered cubic crystal to another one with a different lattice constant

identified for systems similar to the ones discussed above [19, 20, 21, 22]. Similar to what is shown in Figure 1, also the endpoint of the phase-transition line for the HCY exhibits a critical attraction constant Γ^c that increases with decreasing range parameter δ . However, the value Γ^c for phase transitions of the SWS was found practically independent of δ [20]. Contrary to this finding for the crystal-crystal transition, the endpoint of the glass-glass transition line of the SWS behaves quite similar to what is found for the HCY.

Summarizing, one can conclude that the MCT predictions for the dynamics near an A_4 singularity are rather robust. At the present state of discussion, one can use any of the so far studied models to predict data semiquantitatively. Two reservations are required. First, the quality of the theories applied for the evaluation of the structure factors S_q is not known for the high-density regime of interest. The S_q are, however, the essential input functions for all quantitative considerations. Second, the range of validity of the basic MCT equations of motion are not understood, not even qualitatively. Quantitative results of MCT have been tested with encouraging outcome for the hard-sphere system [23], binary Lennard-Jones systems [24], and silica [25]. It remains to be tested by experiment or computer simulation whether or not the theory can also describe the systems studied in this paper.

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Appendix A. Structure Factors

For the calculation of the structure factors we use a scheme developed earlier for the SWS [11]. The short-ranged attraction of the potential from Equation (4) added to the hard core is treated in mean-spherical approximation and the resulting equations are expanded in the small parameter δ . The structure factor is expressed in terms of Baxter's factor function $Q(r)$ [26],

$$S_q^{-1} = \hat{Q}(q)\hat{Q}(q)^*, \quad (\text{A.1})$$

$$\hat{Q}(q) = 1 - 2\pi\rho \int_0^\infty dr \exp[iqr]Q(r). \quad (\text{A.2})$$

In the leading-order approximation, one gets a shifted parabola within the hard core, $0 \leq r \leq 1$,

$$Q(r) = \frac{a}{2}(r^2 - 1) + b(r - 1) + \frac{K}{n}, \quad (\text{A.3})$$

and a polynomial within the attraction shell, $1 \leq r \leq (1 + \delta)$:

$$Q(r) = \frac{K}{n} \left(\frac{1 + \delta - r}{\delta} \right)^n, \quad 1 \leq r \leq 1 + \delta. \quad (\text{A.4})$$

Here, the hard-core diameter d is used as unit of length. For $r > (1 + \delta)$, the factor function is zero. The various constants abbreviate $K = \Gamma\delta$,

$$a = \frac{1 + 2\varphi}{(1 - \varphi)^2} - \frac{12\varphi}{(1 - \varphi)} \frac{K}{n}, \quad b = \frac{-3\varphi}{2(1 - \varphi)^2} + \frac{6\varphi}{(1 - \varphi)} \frac{K}{n}. \quad (\text{A.5})$$

The limit $\delta \rightarrow 0$ can be carried out in Equations (A.3-A.5) in the sense of Reference [10]. It yields the result for S_q used in [3, 4]. However, this procedure appears unjustified. Within the mode-coupling functional, Equation (1b), one needs values of S_q also for large wave-vectors. But the limits $q \rightarrow \infty$ and $\delta \rightarrow 0$ cannot be permuted. Introduction of the cutoff is one way to redefine the model so that the MCT remains meaningful. A more appealing procedure is to consider the δ expansion from Reference [11] and define as Baxter limit the one where terms of order δ^1 are neglected compared to those of order δ^0 . But this is just the approximation defined by Equations (A.3-A.5) that was used in this paper. It is in no respect more complicated to handle than the approximation proposed originally [10].

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